

# SELECTIVE POROSITY DEVELOPMENT BY CALCIUM CATALYZED CARBON GASIFICATION

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## INTRODUCTION

The preparation of activated carbons (AC) with a selective porosity development is of interest to attain an optimum application. Depending on the use of the AC, an essentially microporous material or a wider porosity adsorbent may be necessary.

Porous texture of an AC is mainly determined by: the precursor used, activating mechanism, activating gas, preparation conditions and presence of catalysts [1]. Several studies have shown that catalytic species benefit the preparation of AC as they increase the reaction rate and change the porosity distribution [1,2]. In a previous study [2], it was analyzed the effect of calcium in pore size distribution of the resulting AC as a function of the activating agent ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ). The results showed that calcium-catalyzed carbon activation by  $\text{CO}_2$  produces a remarkable development of the mesoporosity. However, the same effect was not clear when the reaction was performed with steam.

The objective of this study is to analyze calcium-catalyzed carbon activation with steam as a function of steam pressure and in relation with the reaction mechanism [3]. Furthermore, a comparison between catalyzed and uncatalyzed activation depending on the activating gas ( $\text{CO}_2$ , steam) is discussed.

## EXPERIMENTAL

This study concerns a char from almond shell that has a narrow microporosity (carbon B). The char has been oxidized by  $\text{HNO}_3$  at 353 K to increase the calcium exchange capacity (carbon B2). Calcium was loaded by ion exchange from a calcium acetate solution. The sample obtained was dried at 383 K in vacuum. The calcium content is 0.6 wt%.

Catalyzed and uncatalyzed carbon gasification were performed at 1123 K with three  $\text{N}_2$ /steam mixtures (30, 40 and 50 % of steam, 0.1 MPa, 80 ml/min -STP-). Additional experiments were carried out with 100% steam in the

uncatalyzed reaction. Before the reaction, the samples were heated in  $\text{N}_2$  to 1173 K at a heating rate of 5 K/min. The reaction conditions used prevent external diffusion and molecular and Knudsen diffusions within pores to limit gasification rate. However, due to the narrow microporosity of the char, activated diffusion will be important [4]. The burn-off (B.O.) at different times has produced an uncatalyzed set of series of activated carbons for the three steam pressures used and their corresponding series for the catalyzed process. After activation, calcium was extracted by HCl.

Porous texture analysis was carried out by  $\text{N}_2$  adsorption at 77 K and  $\text{CO}_2$  adsorption at 273 K and by mercury porosimetry (CARLO ERBA 2000). Pore size distribution was estimated as described elsewhere [2]. Calcium oxide particle size was measured by  $\text{CO}_2$  chemisorption at 573 K.

## RESULTS AND DISCUSSION

Both catalyzed and uncatalyzed carbon gasification rates increase with  $\text{H}_2\text{O}$  partial pressure. The effective reaction order calculated ( $r \propto p_{\text{H}_2\text{O}}^n$ ), is 0.65 and 0.82 for the uncatalyzed and catalyzed reactions respectively. In spite of the low amount of catalyst present in these samples, it decreases significantly activation time. For example, to obtain a 50% B.O., the uncatalyzed process needs about 12 h whereas the catalyst reduces it to about 8 h. Due to the important contribution of the uncatalyzed reaction, the porosity development for the catalyzed samples will reflect not only the effect of the catalyst.

The results obtained for the uncatalyzed reaction can be summarized as follows. Steam activation produces an important development of super, meso and macropores. The development of wider porosity agrees with the absence of molecular and Knudsen diffusion limitations. Microporosity increases smoothly with B.O., reaching a maximum at about 80% B.O., while for  $\text{CO}_2$  activation a large development of microporosity is observed. The differences found reflect the importance of activated diffusion for steam compared to

CO<sub>2</sub>. Porosity development is independent of the H<sub>2</sub>O partial pressure used. This last observation means that, for the steam pressure range used, the total number of active sites of the carbon is the main factor that controls the results obtained.

Related with the catalyzed reaction, it must be noted that, after the heat treatment in N<sub>2</sub>, the calcium oxide particles have a size of about 2 nm, value larger than the size of the narrow micropores (< 0.7 nm). This means that before reaction, the catalyst is located outside this porosity. After a given B.O., the N<sub>2</sub> isotherms obtained for the sample containing calcium and for the same after extraction, are parallel, indicating that calcium oxide particles block the entrance of the narrow micropores.

Figure 1 presents the N<sub>2</sub> isotherms obtained for samples resulting after catalyzed gasification at different burn-offs under an atmosphere containing a 40% of steam. The adsorption results have been obtained for the samples after calcium extraction. The adsorption capacity increases with burn-off and the steam partial pressure does not modify the porous texture. The isotherms are a combination of type I and II of the BDDT classification. For low burn-offs, the isotherms are of the type I, showing the microporous character of the activated carbons. With increasing burn-off, the knee of the isotherms opens and the slope increases, showing the development of wider porosity. For a 50% burn-off an activated carbon with 1700 m<sup>2</sup>/g results.

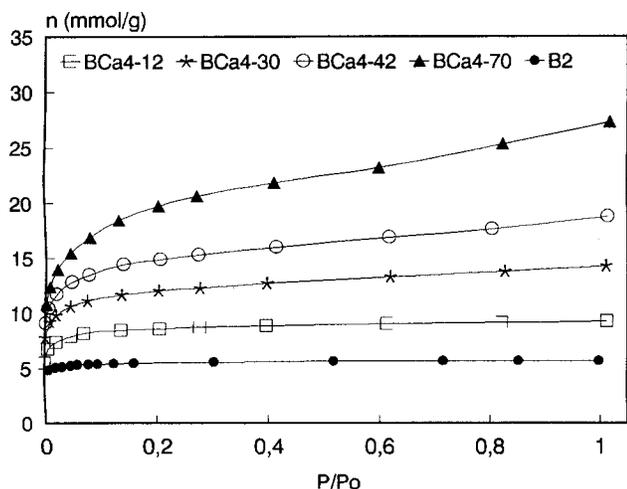


Figure 1. N<sub>2</sub> adsorption isotherms for samples prepared by catalyzed carbon activation.

The comparison of pore size distribution for the catalyzed and the uncatalyzed samples shows that the catalyst only produces differences in the micro and supermicroporosity ranges. Meso and macropore evolution is the same in both cases. Microporosity evolution is similar in both situations, but the values are somewhat larger for the uncatalyzed process. Catalyzed gasification results in an important development of the supermicroporosity (Figure 2). This result is in agreement with the particle size measured for the calcium oxide particles (2 nm). This shows that calcium catalyzed carbon gasification in CO<sub>2</sub> and steam occurs through the calcium-carbon contact, in accordance with the mechanism proposed [3].

#### REFERENCES

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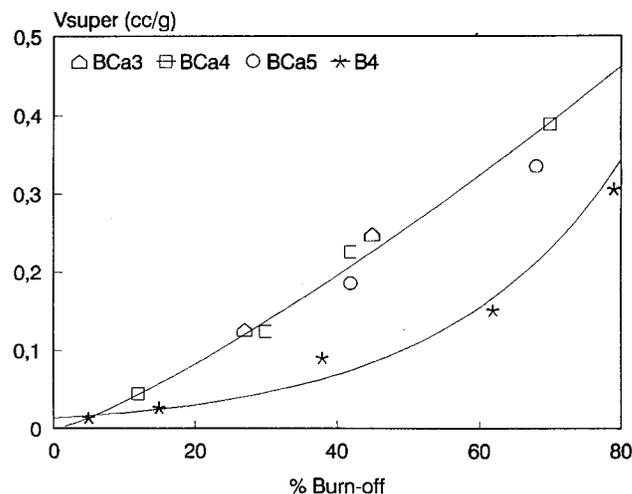


Figure 2. Microporosity evolution for samples activated with and without catalyst.